Development of Gas Separation System by Membrane- Effects of Different Physical Parameters on Membrane Formation

by

Hamdani Saidi, Ramlan Abd. Aziz, Intan Khalida Salleh
Membrane Research Unit
Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia
Jalan Semarak
54100 Kuala Lumpur.

ABSTRACT

Flat sheet cellulose acetate membranes with asymmetric structure were prepared by a wet phase inversion process. In the preparation procedure of phase inversion membranes several parameters determining the structure and properties of the membrane were identified. These parameters are casting solution composition (polymer concentration), solvent evaporation period, precipitation bath composition, annealing temperature and room humidity. In this paper the effect of the first three parameters on the membranes formation were presented. The membranes are characterised in terms of their permeabilities by permeation cell. The membrane structures are studied using scanning electron micrographs. The results showed that polymer concentration, solvent evaporation periods and a precipitation bath composition significantly affect the membrane structures and performance.

ABSTRAK

Membran kepingan rata sellulos asetat yang mempunyai struktur asimmetrik telah disediakan dengan kaedah balikan fasa basah. Dalam proses penyediaan membran balikan fasa, terdapat beberapa faktor yang menentukan struktur dan sifat-sifat membran. Faktor-faktor tersebut adalah komposisi larutan tuangan (kepekatan polimer), masa peruwapan pelarut, komposisi larutan pemendakan, suhu sepuhlendap dan kelembapan bilik. Dalam kertas kerja ini hanya kesan tiga faktor pertama ke atas struktur dan sifat-sifat membran dibentangkan. Sel penelapan digunakan bagi mencirikan kadar kebolehtelapan gas melalui membran sementara pencirian ke atas struktur membran dilakukan dengan menggunakan mikrograf elektron imbasan. Keputusan ujikaji ini menunjukkan kepekatan polimer, masa peruwapan pelarut dan komposisi larutan pemendakan mempengaruhi struktur dan keupayaan membran.

INTRODUCTION

The study of membranes for gas separation has been the focus of active research for over 20 years. With the promise of combining energy efficiency and simplicity, membrane processes can be an attractive solutions for problems encountered in gas separations[1]. Membranes are used in the field of gas separations for recovering hydrogen from process streams, to remove carbon dioxide from methane in enhanced oil recovery and in landfill gas purification, and to produce nitrogen enrichment for blanketing and oxygen enriched air for combustions[2].

A non-porous asymmetric membrane is the most frequently used as either flat-sheet or hollow fiber membrane[1]. This membrane possess an asymmetric cross-section, the top part layer being the selective layer subtended by a porous, non-selective mechanical support. The layers made of the same material. The flat-sheet membrane was first applied in gas separation in 1970 and this membrane was a modified cellulose acetate reverse osmosis membrane of the Loeb-sourirajan type. RO membrane have to be kept wet in order to maintain their permeation performance. To apply this membrane in gas separation, drying methods was developed. The membranes were dried using either freeze drying or solvent exchange method[3]. An asymmetric membrane are classically produced by a phase inversion which is a multistep process involving: solution preparation, film casting, partial solvent preparation, coagulation and sometimes heat post-treatment (Annealing)[4]. In a coagulation bath, the solvent diffuses out of and non-solvent diffuses into the film and the polymer will precipitate forming a membrane. Morphology and permeation properties of the membranes are strictly related to the above preparation step. Cellulose acetate is one of the few polymers currently being used in commercial gas separations. This polymer has been used as a membrane material for many years since it is relatively inexpensive.

In this paper, morphology, permeation properties and mechanical properties of the cellulose acetate based membranes are reported in relation to some preparation variables in the phase inversion process such as casting solution (polymer concentration), exposure or evaporation conditions (time and exposure temperature) and coagulation conditions (additives in the coagulation bath and temperature of the bath)

EXPERIMENTAL

Membranes were prepared by the phase inversion process. The cellulose acetate was dissolved in a mixture of acetone and dimethyl formamide. The polymer concentration was changed as follows: 5%, 10%, 15%, 20%, 25% and 27% wt. Polymer solution were cast at room temperature (23^{o}C) on a glass plate with a knife. After exposure in air for a period varying between 10 and 50 seconds, the plate was immersed in the coagulation bath composed of pure water or water-ethanol mixtures. The membranes were annealed in water at temperature of 85^{o}C.

MEMBRANE CHARACTERIZATION

Permeation studies[5]

The gas permeation rate for different type of membrane was measured using 'permeation cell' which is fabricated to measure pure gas permeation rate using flat sheet membrane under a controlled environment. The gas permeability testing apparatus was filled with a pure gas, namely CO_2 from high-pressure cylinders. The highest pressure was 100 psia. The operating temperatures are in range of 25-60^{o}C.

Then, by measuring the volumetric flow of gas through the membrane, the gas permeation rate was calculated according to the following equation;

$$P/l = Q/(A(P_H-P_L))$$

where P/l is the permeation rate ($cm^3(STP)/cm^2$ s cm Hg), Q is the volumetric flow rate (cm^3/s), A is the membrane area (cm^2), P_H and P_L are feed and permeate pressure (cm Hg) respectively, and l is the membrane thickness.

Determination of the membrane structure[5]

The membrane morphology was examined using a scanning electron microscope (AMRAY 1830I). After the permeability measurement (flat sheet membrane only), the tested membrane was used for the SEM study. For each tested membrane, SEM micrographs of the cross section were taken. Micrographs were taken of samples coated with a 100-300^{o}A thick gold-palladium film. Fractured samples for SEM observations of the membrane cross section were prepared as follows. A small piece of the tested membrane was cut and conditioned in liquid nitrogen. The membrane was carefully fractured at liquid nitrogen temperature. SEM pictures of the cross section of the fractured samples were taken.

RESULTS AND DISCUSSION

Efect of evaporation period[6]

Increasing the evaporation period of the solvent have a significant effect on the structure and properties of the final membrane. Table 1 summarised the result of this effect. Figure 1a-c show graphs of permeation rate versus evaporation period for membrane which were evaporated at 10, 30, 40 and 50 seconds. From these graphs, it shows that as evaporation period increases the gas permeation rate is decreases. This observation can be explained by an increase in the polymer concentration at the surface of a cast film as it evaporated . Solvent evaporation also lead to a significant change in the casting composition since solvent mixtures with significant differences in their boiling point were used, acetone (b.p 56.2 ^{o}C) and dimethyl formamide (b.p. 105^{o}C).The evaporation procedure may change the ratio of the two solvents in the casting solution at the membrane surface, thus affecting the structure and transport properties of the final membrane rather drastically. Figure4a-d show Scanning Electron Micrographs of the resulting membranes. From these micrographs, it may be noticed that the membrane with longer evaporation period (40-50 secs) has thicker skin (top layer) compared to the short evaporation period. These membranes also has support with less pores but larger pores. While the pores in the membranes with short evaporation period are mostly made of open cells, the pores in the membrane with longer evaporation period are a mixture of open cells and closed cells.

Effect of ethanol concentration in Precipitation Medium[7]

Ethanol concentration, 5%, 10%, 15% and 20%, permeation rate, operation pressure and temperature are summarized in Table 2. Figure 2a-c show the effect of ethanol concentration in the precipitation medium on CO_2 permeation performance. These graph show that as ethanol concentration in the precipitation medium increases, permeability also increases. Alcohol has a great effect on the porosity of the membrane. As its concentration increases in the precipitation medium, the effect changes from that of a swelling agent to that of a non-solvent. As a swelling agent, alcohol tends to promote an increasing number of smaller-size droplets resulting in finer precipitating of the polymer with smaller-size pores, whereas alcohol as a non-solvent tends to increase the porosity of the membrane. Figure 5a-d show the micrographs of the resultant membranes.

Effect of polymer concentration in the casting solution[8]

At 5% polymer concentration no membrane was formed. This is due to the casting solution which is too fluid. The primary gel is subjected to distruption by both the weight of the non-solvent and the currents coming into play during immersion. For polymer concentration of 10-25%, typical membrane were obtained but with slightly different structure and performance. At 27% polymer concentration a completely different properties were found. The effect of increasing concentration of cellulose acetate in the casting solution on the performance of the membranes is shown in Table 3 and Figure 3a-e. From these graphs (permeability versus polymer concentration), it show that membranes that have polymer concentration of 20-25% is the optimum concentration for best membrane formation. At 27% of polymer concentration permeability is decreased due to the thicker skin of the membrane (active layer). The concentration of CA determines the viscosity of the casting solution. Too high CA concentration i.e <27% causes the skin to thicken. The scanning electron micrographs of Figure 6a-e show the cross section of five membranes of different polymer concentration. As it can be seen micrographs a to d produced about the same structure except finger-like structure is found more for membrane c and d. Membrane 6e (27%) produced a membrane with a very thick skin and spongy-like structure.

CONCLUSION

In conclusion, the experimental data and micrographs strongly support that solvent evaporation period, precipitation medium and casting solution composition greatly influenced the membrane structure and performance. As the solvent evaporation period increases, permeability decreases. With respect to ethanol concentration in precipitation medium, the results show that permeability increases with the increase of ethanol concentration. By varying the polymer concentration in the casting solution, it was found that 20-25% of CA is the optimum concentration for best membrane formation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the Ministry of Science, Technology and Environment, Government of Malaysia through IRPA for generously funding this project. Acknowledgement is also made to Research and Consultancy Unit (UPP) and Faculty of Chemical& Natural Resources Engineering of UTM for their contribution and support.

REFERENCE

1. Ph.D Thesis Saidi H.(1988). An experimental study of the effects of operating conditions on permeation rates and selectivities, and their interpretations using 'Dual-sorption' and 'Free-Volume' theories.

2. Rautenbach R., Ablbrecht.(1989). Special Application of Pressure Driven Membrane Process. Pages 273-331 in Membrane Process.

3. Minhas B.S., Matsuura T. and Sourirajan S. (1985). Solvent-Exchange drying of Cellulose Acetate Membranes for Separation of Hydrogen-Methane Gas

Mixtures. Pages 452-466 in Reverse Osmosis and Ultrafiltration, American Chemical Society, Washington D.C.

4. Kesting R,(1984) Phase Inversion Membranes. Pages 131-164 in Material Science of Synthetic Membrane,American Chemical Society,Washington D.C.

5. Hamdani Saidi, Ramlan Aziz, I.K. Salleh, H.Hassan.Development of Gas Separation System by Membranes- Preliminary Results of Membrane Characterization, presented at IRPA seminar, UUM, Sintok, Kedah, December, 1991.

6. Ibrahim N.A (1991). Kesan Masa Peruwapan Pelarut Ke atas Struktur Membran, B. Eng. Thesis. The Chemical & Natural Resources Engineering Faculty, UTM, KL.

7. Shafei A.N. (1991). Kesan kepekatan Ethanol dalam larutan Pemendakan ke atas sifat Membran Selulos Asetat, B. Eng. Thesis. The Chemical & Natural Resources Engineering Faculty, UTM, KL.

8. Chai Y.F (1991). Kesan kepekatan Polimer dalam Larutan Polimer terhadap Fluks Membran, B. Eng. Thesis. The Chemical & Natural Resources Engineering Faculty, UTM, KL.

Table 1: Effect of solvent evaporation period on membrane performance

tw (s)	T (oC)	Pressure			
		* 70	80	90	100
		** 362	414	465	517
		***			
10	25	7.3016E-03	6.9781E-03	6.3213E-03	5.9414E-03
	30	8.0427E-03	7.7780E-03	7.5623E-03	7.1057E-03
	40	8.6746E-03	8.4347E-03	8.2772E-03	8.1863E-03
30	25	5.0551E-03	4.7616E-03	4.4968E-03	3.9452E-03
	30	5.1103E-03	4.8320E-03	4.5589E-03	4.3079E-03
	40	5.2341E-03	5.0475E-03	4.9660E-03	4.8830E-03
40	25	4.3720E-03	4.3553E-03	3.9530E-03	3.9196E-03
	30	4.4429E-03	4.3860E-03	4.0887E-03	4.0210E-03
	40	4.6293E-03	4.4961E-03	4.0929E-03	4.0758E-03
50	25	1.6518E-03	1.5374E-03	1.4785E-03	1.4473E-03
	30	1.7140E-03	1.6129E-03	1.5182E-03	1.5018E-03
	40	2.0044E-03	1.9872E-03	1.9247E-03	1.7315E-03

Table 2 : Effect of ethanol gelation medium on membrane performance

(P) x 10-3 (Psia) (cm^3(STP)/cm^2.s.mmHg)	PH
T = 25°C	
1.5788	100
1.5790	90
1.6013	80
1.7357	70
T = 30°C	
1.5004	100
1.5370	90
1.6129	80
1.7069	70
T = 40°C	
1.6939	100
1.8937	90
1.9298	80
1.9676	70

(P) x 10-3 (Psia) (cm^3(STP)/cm^2.s.mmHg)	PH
T = 25°C	
3.8945	100
3.9278	90
4.3174	80
4.4681	70
T = 30°C	
3.9976	100
4.0510	90
4.4322	80
4.4771	70
T = 40°C	
3.9987	100
4.0365	90
4.5296	80
4.5350	70

Table 2 : Effect of ethanol gelation medium on membrane performance

(P) x 10-3 (Psia) (cm^3(STP)/cm^2.s.mmHg)	PH
T = 25°C	
3.9219	100
4.5053	90
4.8639	80
5.0209	70
T = 30°C	
4.2026	100
4.6003	90
4.8309	80
5.1609	70
T = 40°C	
4.7534	100
4.9660	90
4.9686	80
5.1286	70

(P) x 10-3 (Psia) (cm^3(STP)/cm^2.s.mmHg)	PH
T = 25°C	
5.3724	100
6.3388	90
6.9160	80
7.2092	70
T = 30°C	
6.5121	100
6.7660	90
7.0258	80
7.7576	70
T = 40°C	
7.6097	100
8.0533	90
8.2612	80
,8.3128	70

Table 3: Effect of polymer concentration on membrane performance.

Pressure = 50 Psig Temperature = 25 deg.C		Pressure = 80 Psig Temperature = 25 deg.C		Pressure = 100 Psig Temperature = 25 deg.C	
10%	205.9943	10%	284.7747	10%	407.2379
15%	435.4998	15%	1667.462	15%	2402.403
20%	2058.551	20%	2804.296	20%	3551.246
25%	3231.524	25%	3639.122	25%	3639.122
27%	0	27%	0	27%	321.032

Pressure = 120 Psig Temperature = 25 deg.C		Pressure = 150 Psig Temperature = 25 deg.C	
10%	502.4994	10%	796.9162
15%	3122.834	15%	3722.641
20%	4036.697	20%	4262.681
25%	4285.395	25%	6014.931
27%	332.664	27%	414.6898

Figure 1a : Effect of evaporation period on permeation rate at 25 deg.C

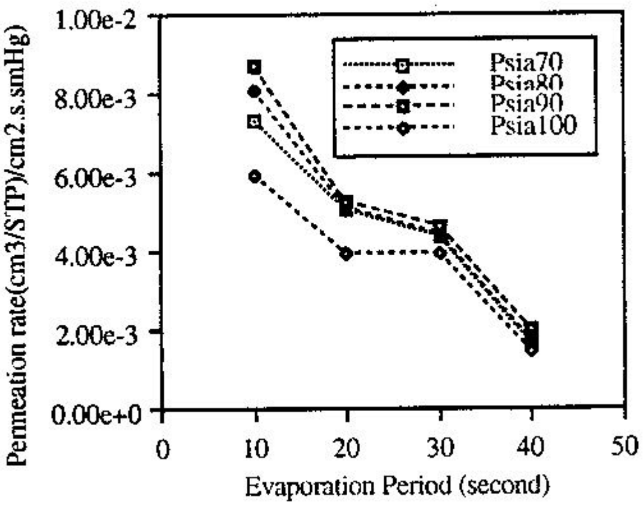


Figure 1b : Effect of evaporation period on permeation rate at 30 deg.C

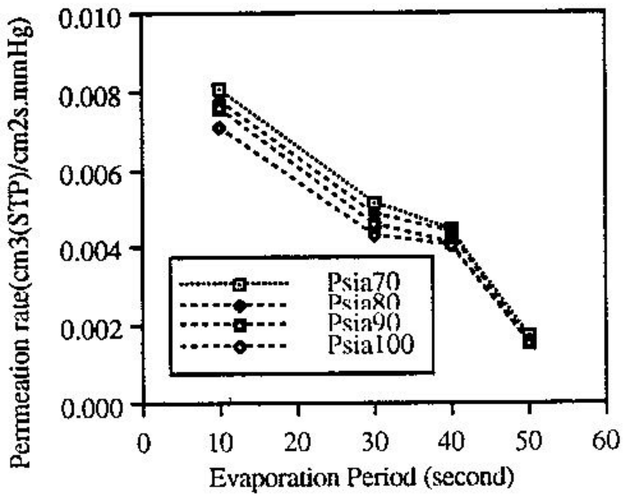


Figure 1c : Effect of evaporation period on permeation rate at 40 deg.C.

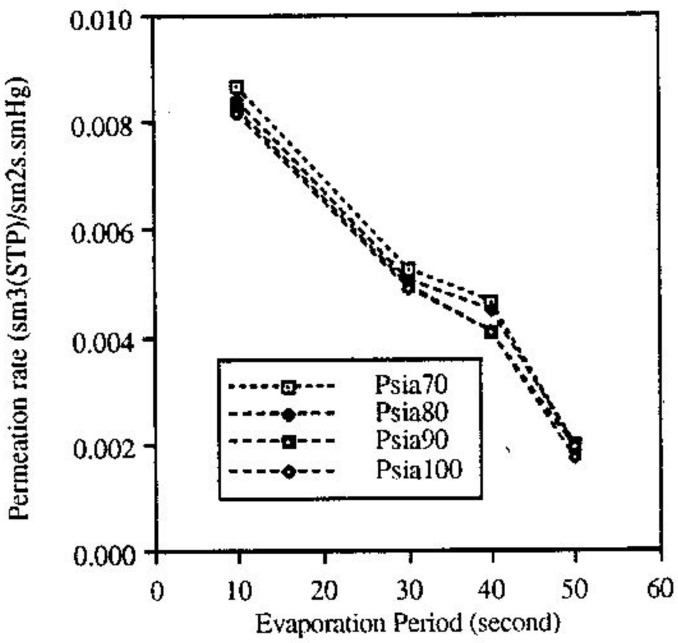


Figure 2a : Effect of ethanol concentration as gelation medium permeation rate at 25 deg.C.

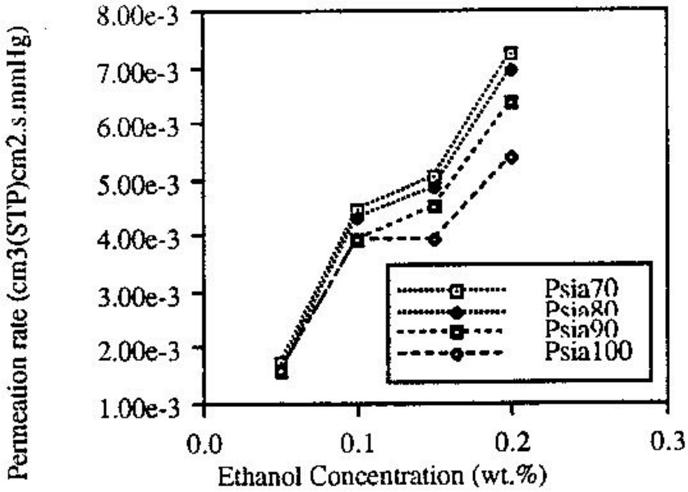


Figure 2b : Effect of ethanol concentration as gelation medium permeation rate at 30 deg.C.

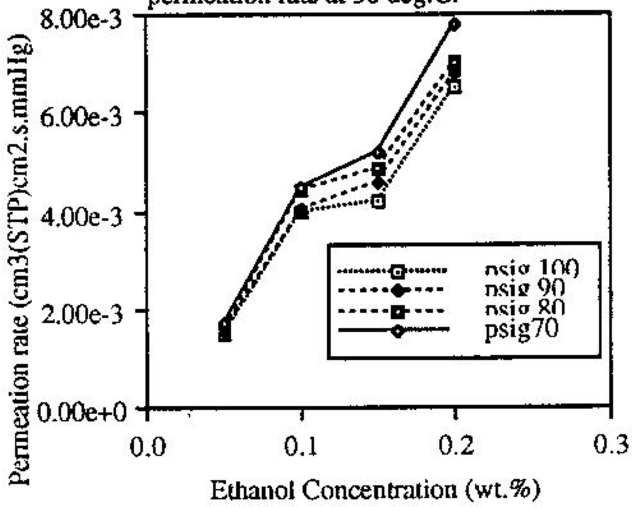


Figure 2c : Effect of ethanol concentration as gelation medium on permeation rate at 40 deg.C.

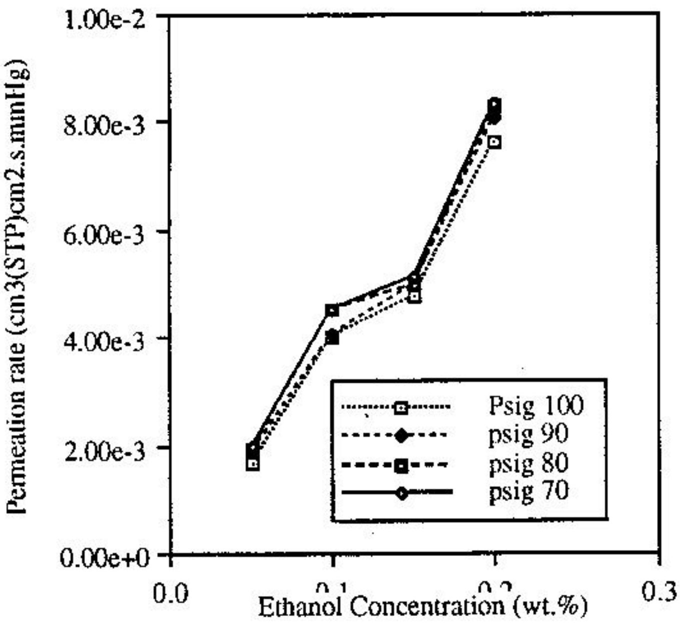


Figure 3a : Effect of polymer concentration in the casting solution on the gas permeability (T=25 deg.C, P= 50 Psig)

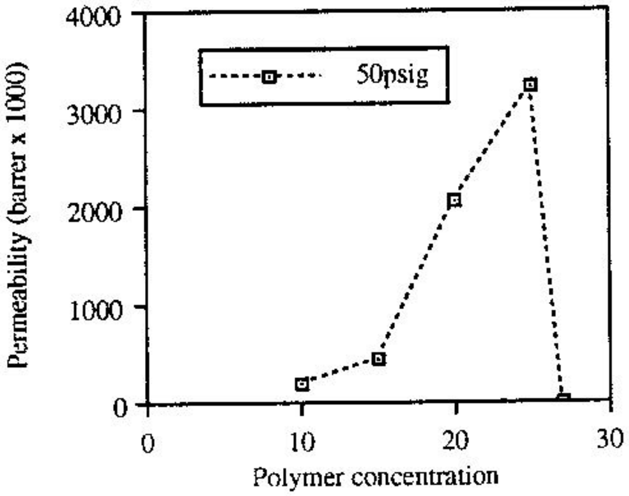


Figure 3b: Effect of polymer concentration in casting solution on gas permeability (25 deg. C, P = 80 Psig)

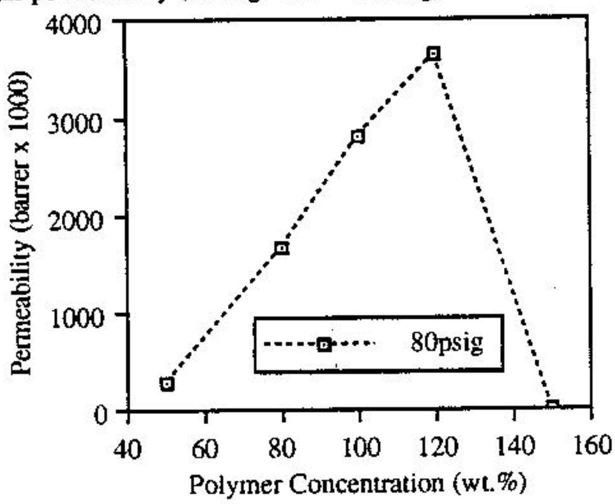


Figure 3c: Effect of polymer concentration in casting solution on gas permeability (25 deg.C, P=100Psig)

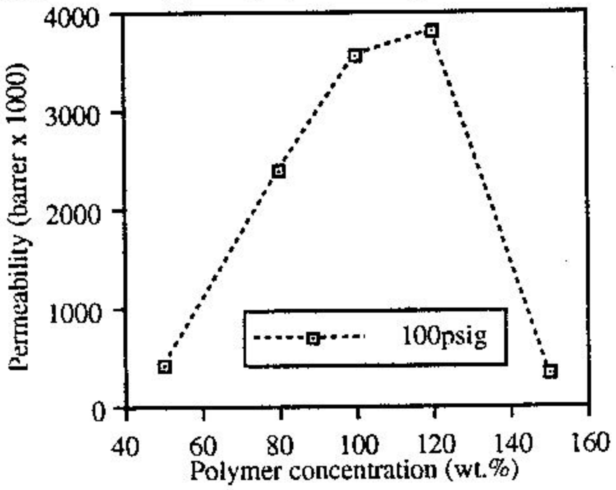


Figure 3d :Effect of polymer concentration in the casting solution on gas permeability (T=25 deg. C, P=120Psig)

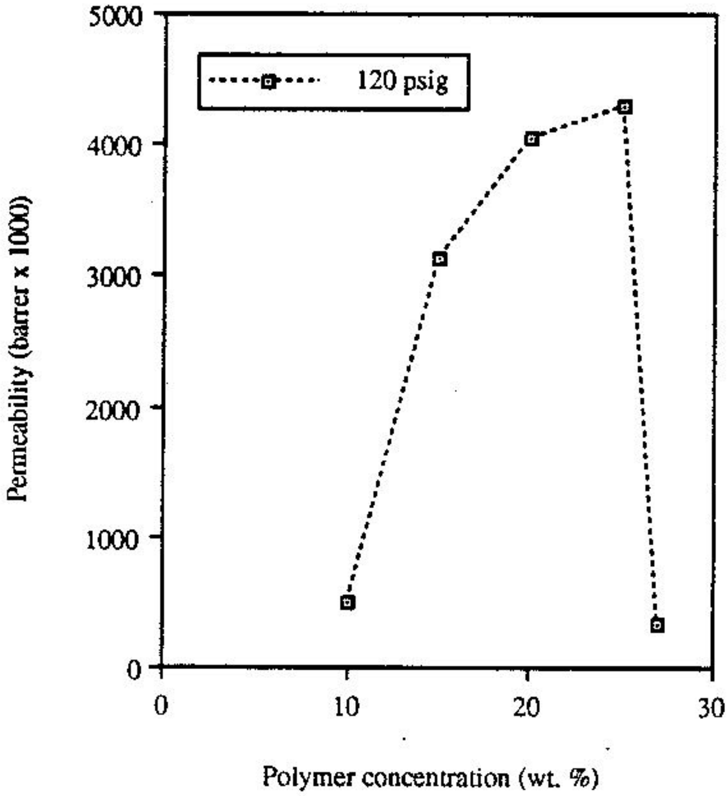
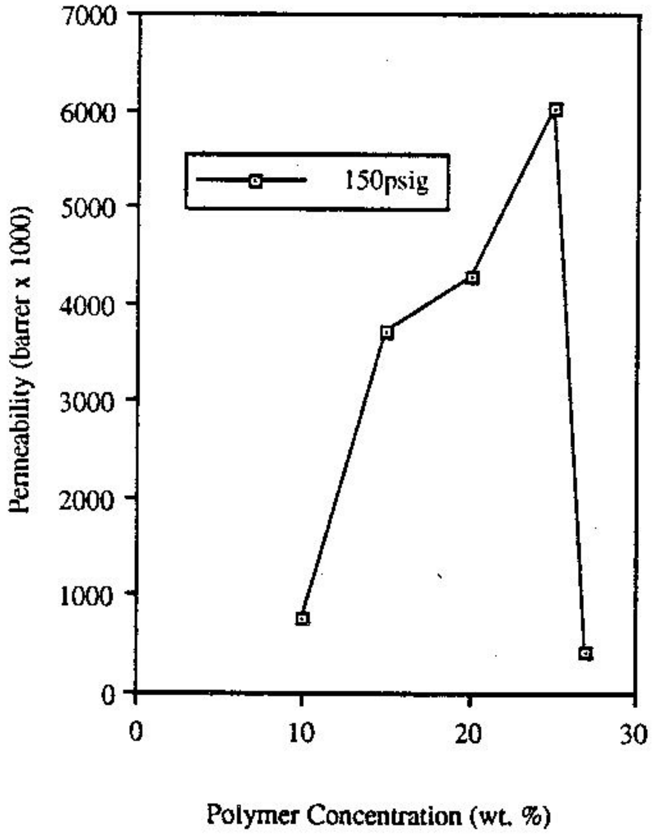
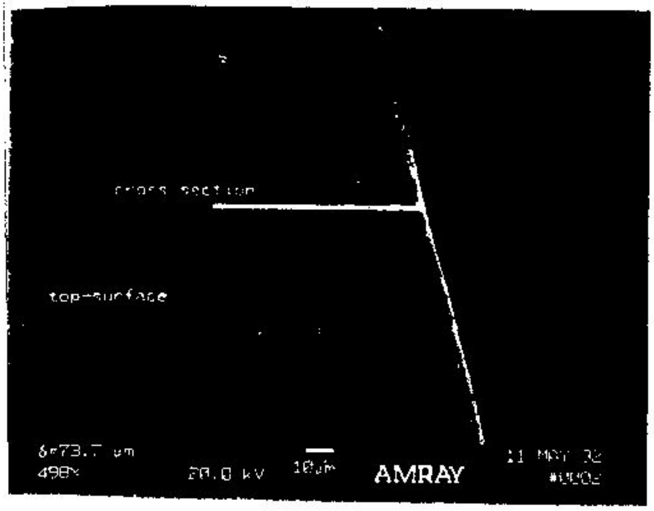
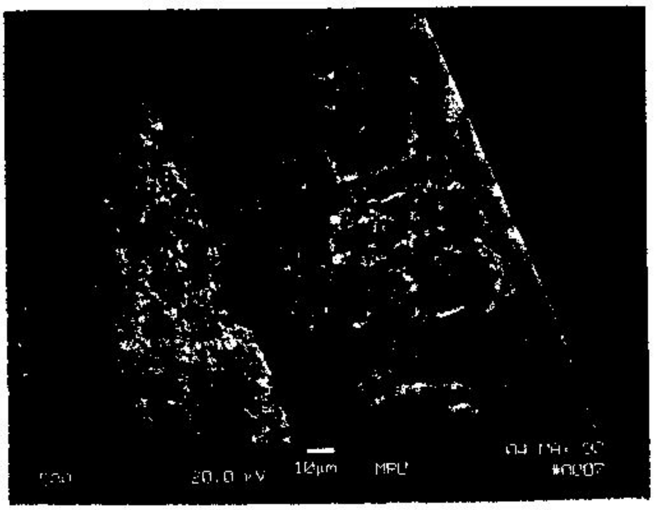


Figure 3e :Effect of polymer concentration in casting solution on gas permeability (25 deg.C, P=150Psig).

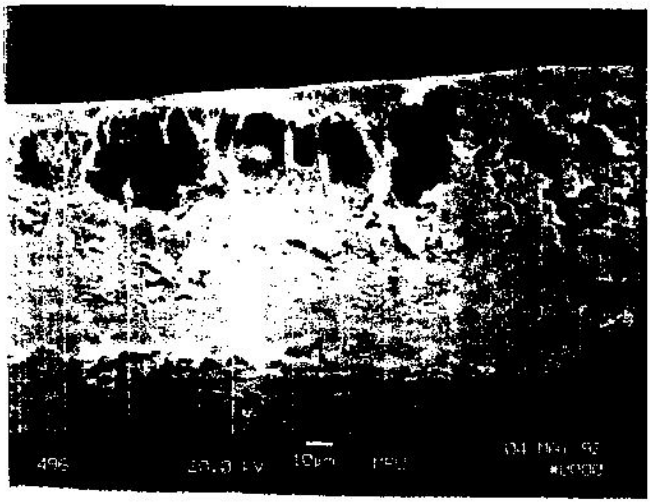


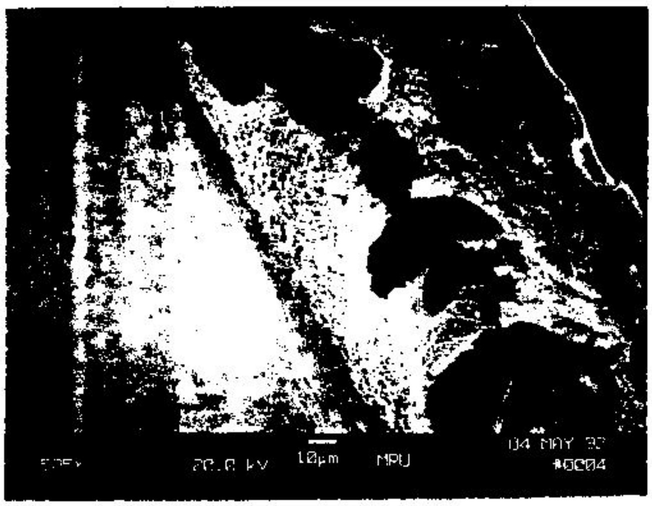




4a

4b





4c

4d

Figure 4: Scanning electron micrographs of membrane cross section prepared from cellulose acetate in acetone and evaporated at various period prior to precipitation in water at room temperature.
4a) 10 seconds
4b) 30 seconds
4c) 40 seconds
4d) 50 seconds

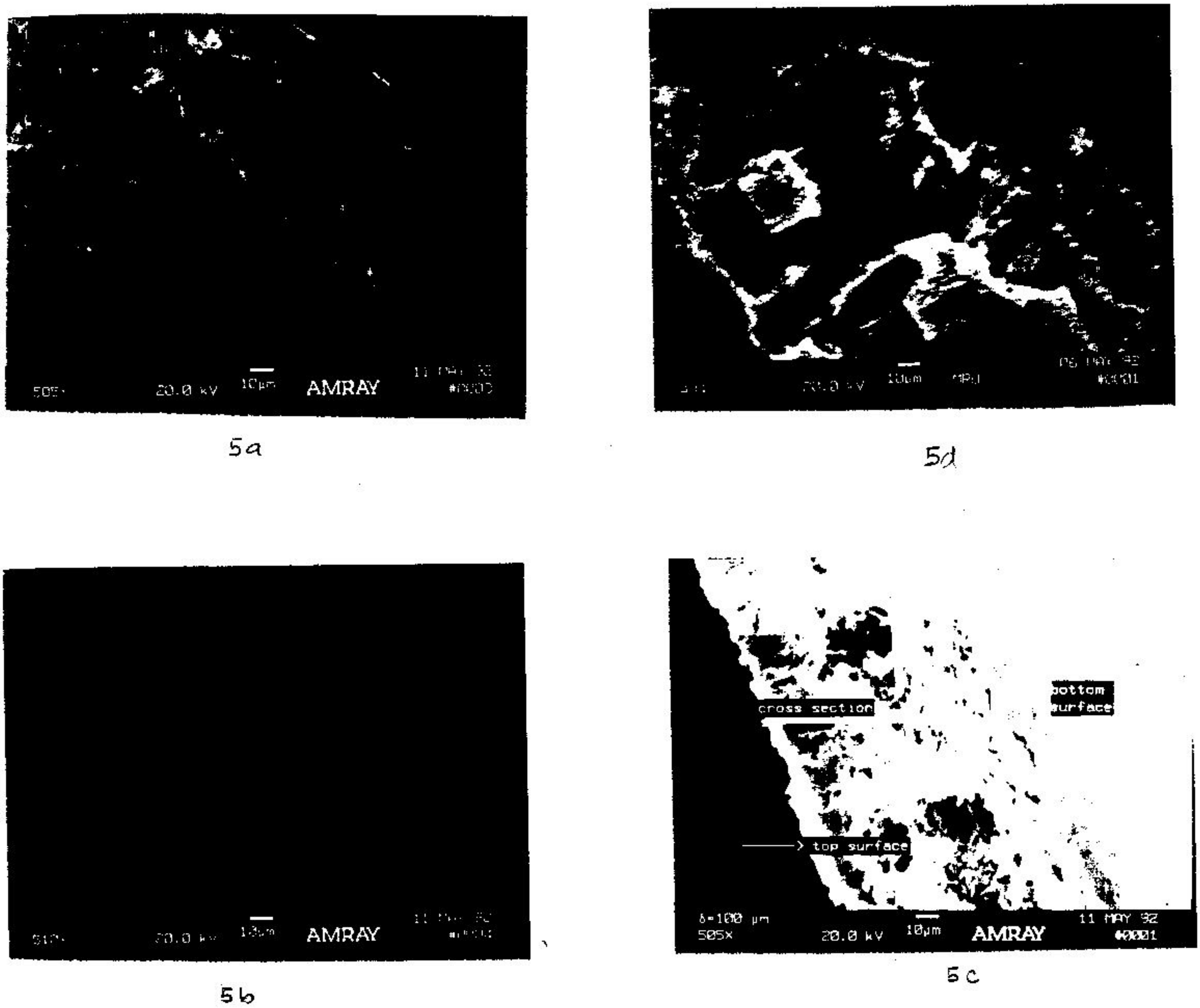
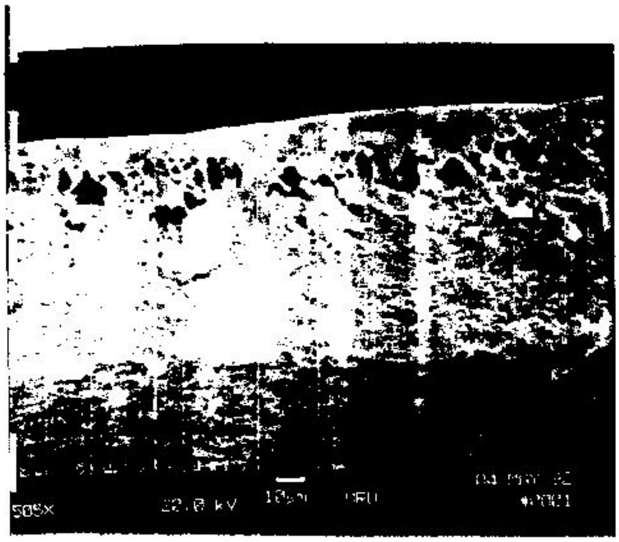


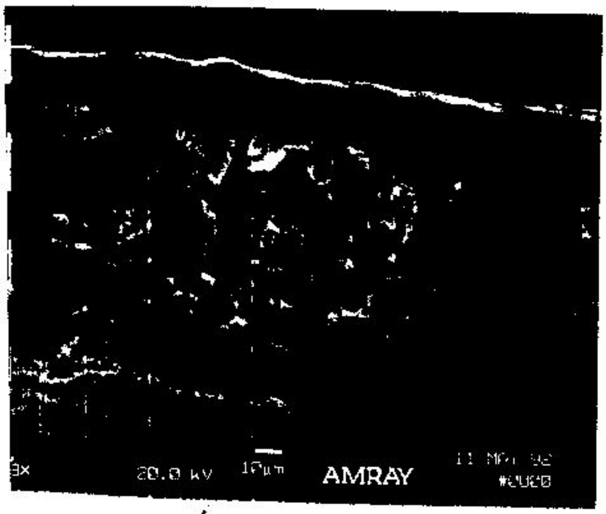
Figure 5: Scanning electron micrographs of membrane cross sections prepared from a casting solution of 25% CA in acetone precipitated at room temperature in different concentration of ethanol.

5a) 5%
5b) 10%
5c) 15%
5d) 20%

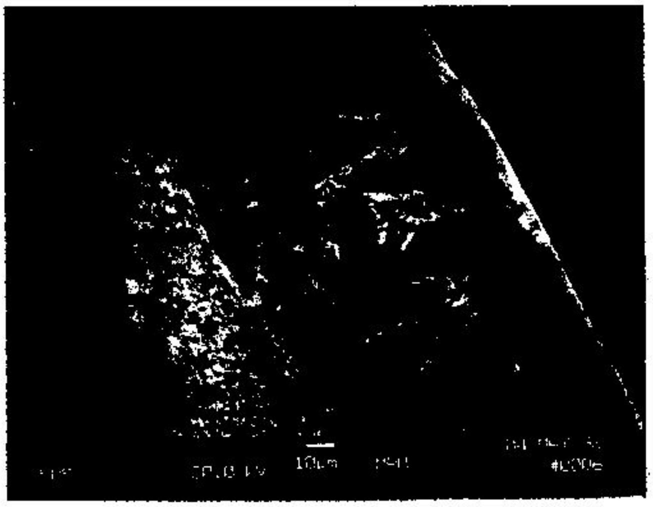


6a

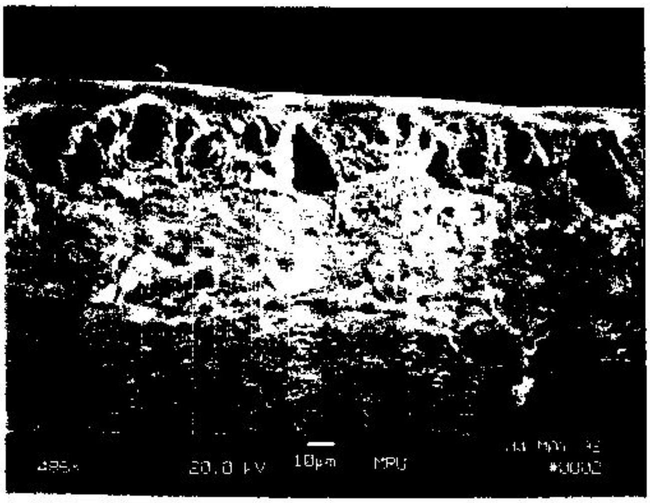
6e



6b



6d



6c

Figure 6: Scanning electron micrographs of membrane cross section prepared from various cellulose acetate concentrations in acetone by precipitated in water at room temperature.

6a) 10%
6b) 15%
6c) 20%
6d) 25%
6e) 27%